

(19)



Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

EP 1 063 270 A2

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:

27.12.2000 Bulletin 2000/52

(51) Int. Cl.⁷: **C09D 183/04, C09J 183/04**

(21) Application number: **00304873.3**

(22) Date of filing: **08.06.2000**

(84) Designated Contracting States:

**AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU
MC NL PT SE**

Designated Extension States:

AL LT LV MK RO SI

(30) Priority: **21.06.1999 US 337444**

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(54) **Adhesion primer for use with RTV silicones**

(57) A low volatile organic compound primer composition suitable for use with room temperature vulcanizable silicones, comprising a polyorganosiloxane resin, an acrylic resin, an organotitanate, a silane or partial hydrolyzate thereof and an organic liquid in amount effective to dissolve the other components of the primer composition that provides improved adhesion to diverse substrates.

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Description

[0001] The present invention relates to primer compositions, more specifically to primer compositions for bonding room temperature vulcanizable ("RTV") silicone elastomers to diverse substrates.

[0002] The use of primers for the purpose of improving the adhesion of RTV silicone elastomers are known, see for example, U.S. Patent Nos. 4,681,636 and 4,749,741.

[0003] U.S. Patent No. 4,147,685 discloses a primer composition that is a reaction product of methyl or butyl methacrylate and an acrylate functional silane in an organic solvent. The reaction product is made by heating the primer ingredients at a temperature of 50 to 80°C in the presence of a peroxide catalyst. The compositions disclosed in the '685 patent exhibit improved adhesion to plastics, but have been found to be deficient when the solids content of the primer as unreacted acrylate functional silane monomer is less than 10%. Additionally, the compositions disclosed in the '685 patent exhibit high volatile organic compounds (VOCs).

[0004] What is needed in the art is a primer composition that provides improved adhesion to diverse substrates, particularly concrete and plastics, while exhibiting lower VOCs.

[0005] The present invention is directed to a low VOC primer composition suitable for use with room temperature vulcanizable silicone elastomers, comprising the product formed by combining:

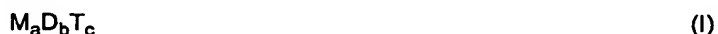
- (i) a polyorganosiloxane resin;
- (ii) an acrylic resin;
- (iii) an organotitanate;
- (iv) a silane or partial hydrolyzate thereof; and
- (v) an organic liquid in amount effective to dissolve components (i), (ii), (iii) and (iv) of the primer composition.

[0006] The primer composition of the present invention provides improved adhesion to diverse substrates, particularly concrete.

[0007] In a preferred embodiment, the primer composition of the present invention comprises, based on 100 parts by weight ("pbw") of the primer composition, from 1 pbw to 80 pbw, more preferably from 5 pbw to 50 pbw, still more preferably from 15 pbw to 25 pbw, of the polyorganosiloxane resin; from .1 pbw to 25 pbw, more preferably from .5 pbw to 15 pbw, still more preferably from 1 pbw to 10 pbw, of the acrylic resin; from 1 pbw to 25 pbw, more preferably from 5 pbw to 20 pbw, still more preferably from 8 pbw to 15 pbw, of the organotitanate; from .01 pbw to 20 pbw, more preferably from .1 pbw to 10 pbw, still more preferably from .2 pbw to 5 pbw, of the silane or partial hydrolyzate thereof; from .5 pbw to 95 pbw, more preferably from 25 pbw to 85 pbw, still more preferably from 50 pbw to 75 pbw, of the organic liquid.

Polyorganosiloxane Resin

[0008] Polyorganosiloxane resins that are suitable as the polysiloxane resin component of the composition of the present invention are those resins containing structural units according to the formula (I):



wherein:

M is $R^1 R^2 R^3 SiO_{1/2}$;

D is $R^4 R^5 SiO_{2/2}$;

T is $R^6 SiO_{3/2}$;

R^1, R^2, R^3, R^4, R^5 and R^6 are each independently hydrogen or monovalent hydrocarbon radicals; and

a, b and c are each integers, wherein $1 \leq a \leq 10,000$, $1 \leq b \leq 10,000$ and $1 \leq c \leq 10,000$.

[0009] Suitable monovalent hydrocarbon radicals include monovalent acyclic hydrocarbon radicals, monovalent alicyclic hydrocarbon radicals and monovalent aromatic hydrocarbon radicals.

[0010] As used herein, the terminology "acyclic hydrocarbon radical" means a straight chain or branched hydrocarbon radical, preferably containing from 2 to 24 carbon atoms per radical, which may be saturated or unsaturated. Suitable monovalent acyclic hydrocarbon radicals include, for example, methyl, sec-butyl, tert-butyl, octyl, decyl, dodecyl, cetyl, stearyl, propenyl, and butynyl.

[0011] As used herein, the terminology "alicyclic hydrocarbon radical" means a radical containing one or more saturated hydrocarbon rings, preferably containing from 4 to 10 carbon atoms per ring, per radical which may optionally be substituted on one or more of the rings with one or more alkyl or alkylene groups, each preferably containing from 2 to

6 carbon atoms per groups and which, in the case of two or more rings, may be fused rings. Suitable monovalent alicyclic hydrocarbon radicals include, for example, cyclohexyl, cyclooctyl.

[0012] As used herein, the term "aromatic hydrocarbon radical" means a hydrocarbon radical containing one or more aromatic rings per radical, which may optionally be substituted on the one or more aromatic rings with one or more alkyl or alkylene groups, each preferably containing from 2 to 6 carbon atoms per group, or other functional groups and which, in the case of two or more rings, may be fused rings. Suitable monovalent aromatic hydrocarbon radicals include, for example, aryl radicals such as, for example, phenyl, naphthyl and aralkyl, such as, for example, phenethyl.

[0013] In a preferred embodiment, R^1 , R^2 , R^3 , R^4 and R^5 are each independently (C_1 - C_8)alkyl, aryl or aralkyl.

[0014] In a more highly preferred embodiment, R^1 , R^2 , R^3 , R^4 and R^5 are each independently methyl, propyl, octyl, phenyl or diphenyl.

Acrylic Resin

[0015] Acrylic resins that are suitable as the acrylic resin component of the composition of the present invention comprise first repeating units derived from one or more monomers selected from (meth)acrylic ester monomers, (meth)acrylic acid monomers and (meth)acrylamide monomers and, optionally, second repeating units derived from one or more monoethylenically unsaturated monomers copolymerizable therewith. As used herein, the term "(meth)acrylic" refers collectively to acrylic and methacrylic, "(meth)acrylate" refers collectively to acrylates and methacrylates, and the term "(meth)acrylamide" refers collectively to acrylamides and methacrylamides.

[0016] Suitable (meth)acrylic ester monomers include, for example, alkyl (meth)acrylate monomers, preferably (C_1 - C_8)alkyl (meth)acrylate monomers such as, for example, methyl methacrylate, butyl acrylate, ethylhexylmethacrylate; hydroxy(C_1 - C_8)alkyl (meth)acrylate monomers such as, for example, hydroxyethyl methacrylate; (C_4 - C_8)cycloalkyl (meth)acrylate monomers such as, for example, cyclohexyl methacrylate. Suitable (meth)acrylic acid monomers include, for example, acrylic acid, methacrylic acid. Suitable (meth)acrylamide monomers include acrylamide and methacrylamide. Suitable copolymerizable monomers include, for example, monoethylenically unsaturated carboxylic acids such as, for example, itaconic acid; maleimide monomers such as, for example, N-alkyl maleimides, N-aryl maleimides, maleic anhydride, vinyl esters such as, for example, vinyl acetate, vinyl versatate and vinyl propionate.

[0017] In a preferred embodiment, the acrylic resin comprises an acrylic resin selected from poly(methyl methacrylate), poly(acrylonitrile), poly(acrylamide), poly(acrylic acid), and poly(methacrylic acid).

[0018] In a preferred embodiment, the acrylic resin has a weight average molecular weight of from 40,000 to 250,000 grams per mole ("g/mol"), more preferably from 75,000 to 200,000 g/mol, and still more preferably from 90,000 to 150,000 g/mol.

[0019] In a preferred embodiment, the acrylic resin comprises a resin selected from polymethylmethacrylate, polyacrylic acid, polyacrylamide, polymethacrylic acid or polyacrylonitrile. In a most preferred embodiment, the acrylic resin is Paraloid® B-72 acrylic resin (sold by Rohm and Haas Company).

Organotitanate

[0020] Organotitanates that are suitable, as the organotitanate component of the composition of the present invention include, for example, organotitanate esters, titanium complexes, titanium chelate compounds, partially alkoxytated partial chelates of titanium, as well as partial hydrolysis-condensation products of any of these compounds.

[0021] In a preferred embodiment, the organotitanate component is an organotitanate ester according to the structural formula:



wherein each R^7 is independently (C_1 - C_8)alkyl.

[0022] Preferably the organotitanate component comprises an organotitanate ester selected from the group consisting of tetrabutyl titanate, tetramethyl titanate, tetraisopropyl titanate, ethylmethyldibutyl titanate, tetraoctyl titanate, and tetraethylhexyl titanate. More preferably the organotitanate comprises tetrabutyl titanate.

Silane

[0023] Silanes are well known in the art. Silanes that are suitable as the silane component of the composition of the present invention are those that liberate alcohol upon hydrolysis. Examples of suitable silanes include tetraalkoxysilanes, organotrialkoxysilanes and diorganodialkoxysilanes, as well as partial hydrolyzates of any of these compounds.

[0024] In a preferred embodiment, the silane component of the primer composition of the present invention comprises a tetraalkoxysilane or a partial hydrolyzate thereof. More preferably, the silane component comprises a

tetraalkoxysilane selected from the group consisting of tetraethoxy silane, tetrapropoxy silane, polyethyl silicate and polypropyl silicate. Even more preferably, the silane component comprises polyethyl silicate, a partial hydrolyzate of a silane.

5 Organic Liquid

[0025] Organic liquids that are suitable as the organic liquid component of the composition of the present invention are those organic liquids in which the polyorganosiloxane resin, the acrylic resin, the organotitanate and the silane components of the composition are each soluble.

10 **[0026]** In a preferred embodiment, the organic liquid is a low VOC organic liquid or a blend of two or more low VOC organic liquids selected from lower acyclic and salicyclic hydrocarbons, such as, for example, hexane, isododecane and cyclohexane; aromatic hydrocarbons such as for example, benzene, toluene and xylene; ketones, such as, for example, acetone, methyl ethyl ketone, and methyl isobutyl ketone; halogenated hydrocarbon solvents, such as, for example, trichloroethylene and parachlorobenzotrifluoride. As used herein, "low VOC" means that the volatile organic compound
15 level is less than 350 g/l.

[0027] In a highly preferred embodiment, the organic solvent component comprises parachlorobenzotrifluoride.

[0028] Performance properties of the primer of the present invention compare favorably to those properties of primers with high VOC levels.

20 Other Components

[0029] The primer composition of the present invention, may, optionally, further include other components, such as, for example, stabilizers, colorant and any other components known in the art.

25 **[0030]** In a highly preferred embodiment, the primer composition of the present invention comprises, based on 100 pbw of the primer composition:

(i) from 15 pbw to 25 pbw of an polyorganosiloxane resin;

(ii) from 1 pbw to 10 pbw of an acrylic resin selected from polymethylmethacrylate, polyacrylic acid, polyacrylamide, polymethacrylic acid and polyacrylonitrile;

30 (iii) from 8 pbw to 15 pbw of an organotitanate resin selected from tetrabutyl titanate, tetramethyl titanate, tetraisopropyl titanate, ethylmethyldibutyl titanate, tetraoctyl titanate, and tetraethylhexyl titanate;

(iv) from .2 pbw to 5 pbw of a silane or partial hydrolyzate thereof resin selected from tetraethoxy silane, tetrapropoxy silane, polyethyl silicate and polypropyl silicate; and

(v) from 50 pbw to 75 pbw of an organic liquid resin selected from trichloroethylene and parachlorobenzotrifluoride.

35 Processing and Use

[0031] The primer composition of the present invention is made by mixing and heating the components to provide a homogeneous solution. In a preferred embodiment, the components are mixed together in a particular order, with the
40 polyorganosiloxane added to the solution at a slow rate.

[0032] The primer composition of the present invention is used by applying the primer to a substrate, by for example, brushing or coating the primer onto the substrate, allowing the primer to dry and then applying the RTV silicone elastomer composition, and curing the silicone elastomer. In a preferred embodiment, the primer is brushed onto the substrate.

45 **[0033]** The substrates to which the primer composition of the present invention provides improved adhesion to any difficult substrates, including metals, such as, for example, aluminum and stainless steel, synthetic resins, such as for example, polyvinyl chloride, polyacrylate and acrylic resins, as well as inorganic materials, such as, for example, glasses, concrete and ceramics. In a preferred embodiment, the primer composition will provide improved adhesion to wet pre-cast masonry concrete.

50 **[0034]** The primer composition of the present invention may be used for bonding a curable silicone elastomer composition to a substrate by: a) applying a primer composition to at least a portion of the surface of a substrate, the primer composition comprising: (i) a polyorganosiloxane resin; (ii) an acrylic resin; (iii) an organotitanate; and (iv) a silane or partial hydrolyzate thereof to form a primer layer on the substrate; b) applying a silicone elastomer to a substrate in contact with at least a portion of the primer layer; and c) curing the silicone elastomer.

55 **[0035]** The primer composition of the present invention may be used in an article comprising: a) a substrate; b) a layer of silicone elastomer on at least a portion of the surface of the substrate; c) a layer of a primer composition between at least a portion of the substrate and at least a portion of the silicone elastomer layer, the primer composition comprising: (i) a polyorganosiloxane resin; (ii) an acrylic resin; (iii) an organotitanate; and (iv) a silane or partial hydro-

lyzate thereof.

[0036] The primer composition of the present invention may be used with almost any RTV silicone elastomer compositions that can be used for the desired application.

Example 1

[0037] In a suitable reaction vessel equipped with an agitator, heater, nitrogen purge and vacuum source, was charged an organic liquid (67 pbw parachlorobenzotrifluoride), and an organotitanate (9.7 pbw of tetrabutyl titanate). The contents of the reaction vessel were then gradually heated to 70°C and mixed for ten minutes. A polyorganosiloxane resin (9 pbw polydimethylsiloxane) was then added to the reaction vessel at a rate of 7 pbw per minute). An acrylic resin (13 pbw Paraloid® B-72 acrylic resin) was added and the mixture was agitated for 60 minutes at 70°C. The solution was cooled for twenty to thirty minutes, until the solution temperature reached about 30°C. When the solution reached about 30°C, a silane (1.3 pbw ethyl silicate) was added. The solution was agitated for an additional thirty minutes. The solution was then filtered into a clean container, using caution not to expose the mixture to atmospheric moisture.

Example 2

[0038] Peel adhesion was tested as follows. A thin film of the candidate primer was applied to the surface of the substrate panel with a paint brush. All substrates, except concrete, are cleaned with soap and water and allowed to dry for 25 to 30 minutes prior to use. Approximately 10 to 15 minutes following application of the primer, peel adhesion specimens were prepared using a silicone room temperature vulcanizable composition. A layer of sealant composition was applied to a 1 inch x 8 inch substrate, and about 5 inches of a 1 inch x 12 inch 20 mesh stainless steel screen (that has been primed with a primer and allowed to dry for 30 minutes) was applied over the layer of sealant composition. Another layer of sealant composition was applied over the top of the screen and excess composition was then scraped off, and the samples allowed to cure for 7 days. Additional, identical samples were prepared and cured for 7 days, followed by a 7 day exposure to water at 25°C.

[0039] The screen was folded back over itself and the distal end of the substrate and the distal end of the screen were each clamped in a tensile tester. A razor blade was used to make a cut through the edge of the sealant layer exposed between the substrate and the screen, at an angle of about 45° to the substrate surface, and the specimen was then subjected to tension at a crosshead speed of 2 inches per minute. Two more 45° cuts were made in the sealant, each spaced apart from the immediately preceding cut by about 1 inch. After 7 days of curing on the primed substrates, the specimens were tested for cohesive failure.

[0040] The median pull value of tension, in pounds per inch of sample width, required to cause failure was recorded. The relative amount of cohesive failure was determined by visual inspection of failure surfaces of the test samples, based on the relative amount of originally coated area to which sealant remains bonded.

Materials used:

Primers: SS4044, SS4120, SS4179 are commercially available primers for use with RTV silicone compounds. The primers are available from General Electric Silicones.

RTV Silicone Sealants: The alkoxy RTV used in the example is a one-part silicone sealant, commercially available as Silpruf® Sealant from General Electric Silicones. The acetoxo RTV used in the example is a one-part silicone sealant commercially available as the Contractors SCS1000® Series from General Electric Silicones.

Table I

7 Day Peel Adhesion Test Results ppi/ % cohesive failure					
Silicone/Substrate	Primer of Example 1	No Primer	Primer SS4044	Primer SS4120	Primer SS4179
Alkoxy RTV to Concrete	66/100	54/100	41/100	54/100	54/100
Acetoxo RTV to Polyacrylate	15/70	0/0	6/5	0/0	24/100

Table I (continued)

7 Day Peel Adhesion Test Results ppi/ % cohesive failure					
Silicone/Substrate	Primer of Example 1	No Primer	Primer SS4044	Primer SS4120	Primer SS4179
Alkoxy RTV to Mill Aluminum	54/100	61/95	62/100	67/100	58/100
Acetoxy RTV to Mill Aluminum	19/100	24/40	30/100	26/100	23/100
Alkoxy RTV to PVC	58/100	51/95	37/50	60/100	54/100
Acetoxy RTV to PVC	20/95	0/0	8/5	26/100	24/100
Alkoxy RTV to poly-carbonate	42/100	51/100	36/60	12/10	51/100
Acetoxy RTV to poly-carbonate	22/95	0/0	0/0	3/5	26/100

[0041] The results in Table I show that both peel adhesion and the % cohesive failure generally are higher for samples using the low VOC primer of the invention than for existing primers. VOC level of the new primer of the invention is 337 g/l (below the EPA requirement of 350 g/l).

Table II

7 Day Water Immersion Test Results ppi/ % cohesive failure					
Silicone/Substrate	Primer of Example 1	No Primer	Primer SS4044	Primer SS4120	Primer SS4179
Alkoxy RTV to Concrete	19/30	11/0	23/0	18/5	19/5
Alkoxy RTV to Mill Aluminum	48/95	31/50	54/100	44/80	50/100
Acetoxy RTV to Mill Aluminum	2/5	13/40	7/0	10/10	15/20
Alkoxy RTV to PVC	54/95	14/0	39/85	32/80	61/100
Acetoxy RTV to PVC	19/80	0/0	3/<5	0/0	13/100
Alkoxy RTV to poly-carbonate	48/100	52/100	44/90	36/80	62/100
Acetoxy RTV to poly-carbonate	19/95	0/0	0/0	2/0	13/100

[0042] The results in Table II show that both peel adhesion and the % cohesive failure after 7 day water immersion are also generally are higher for samples using the low VOC primer of the invention than for existing primers.

Claims

1. A primer composition suitable for use with room temperature vulcanizable silicone elastomers, comprising the product formed by combining:

- (i) a polyorganosiloxane resin;
- (ii) an acrylic resin;
- (iii) an organotitanate;

(iv) a silane or partial hydrolyzate thereof; and

(v) an organic liquid in an amount effective to dissolve components (i), (ii), (iii) and (iv) of the primer composition.

2. The primer composition of claim 1, comprising the product formed by combining:

(i) from about 15 to 25 parts by weight of the total composition of a polyorganosiloxane resin;

(ii) from about 1 to 10 parts by weight of the total composition of an acrylic resin;

(iii) from about 8 to 15 parts by weight of the total composition of an organotitanate;

(iv) from about .2 to 5 parts by weight of the total composition of a silane or partial hydrolyzate thereof; and

(v) from about 50 to 75 parts by weight of the total composition of an organic liquid to dissolve components (i), (ii), (iii) and (iv) of the primer composition.

3. The primer composition of claim 1 or claim 2, wherein the organotitanate is tetrabutyl titanate.

4. The primer composition of any preceding claim, wherein the silane is ethyl silicate.

5. The primer composition of any preceding claim, wherein the organic liquid is parachlorobenzotrifluoride.

6. A method for producing a primer composition suitable for use with room temperature vulcanizable silicone elastomers, comprising the steps of:

a) mixing together the components of the primer composition comprising:

(i) a polyorganosiloxane resin;

(ii) an acrylic resin;

(iii) an organotitanate;

(iv) a silane or partial hydrolyzate thereof; and

(v) an organic liquid in an amount effective to dissolve components (i), (ii), (iii) and (iv) of the primer composition; and

b) heating and agitating the composition to form a homogeneous solution.

7. A method for bonding a curable silicone elastomer composition to a substrate comprising:

a) applying a primer composition to at least a portion of the surface of a substrate, the primer composition comprising:

(i) a polyorganosiloxane resin;

(ii) an acrylic resin;

(iii) an organotitanate; and

(iv) a silane or partial hydrolyzate thereof to form a primer layer on the substrate;

b) applying a silicone elastomer to a substrate in contact with at least a portion of the primer layer; and

c) curing the silicone elastomer.

8. An article made by the method of claim 7.

9. An article comprising:

a) a substrate;

b) a layer of silicone elastomer on at least a portion of the surface of the substrate;

5 c) a layer of a primer composition between at least a portion of the substrate and at least a portion of the silicone elastomer layer, the primer composition comprising:

(i) a polyorganosiloxane resin;

10 (ii) an acrylic resin;

(iii) an organotitanate; and

(iv) a silane or partial hydrolyzate thereof.

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(11)

EP 1 063 270 A3

(12)

EUROPEAN PATENT APPLICATION

(88) Date of publication A3:
13.02.2002 Bulletin 2002/07

(51) Int Cl.7: **C09D 183/04, C09J 183/04**

(43) Date of publication A2:
27.12.2000 Bulletin 2000/52

(21) Application number: **00304873.3**

(22) Date of filing: **08.06.2000**

(84) Designated Contracting States:
**AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU
MC NL PT SE**
Designated Extension States:
AL LT LV MK RO SI

(30) Priority: **21.06.1999 US 337444**

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to dissolve the other components of the primer composition that provides improved adhesion to diverse substrates.

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EUROPEAN SEARCH REPORT

Application Number
EP 00 30 4873

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
X	US 3 671 483 A (YOUNG DONALD G) 20 June 1972 (1972-06-20) * claims 1-10 *	1	C09D183/04 C09J183/04
X	US 5 458 980 A (LARSON KENT R) 17 October 1995 (1995-10-17) * claims 1-14 * * column 5, line 31 - line 62 * * column 6, line 27 - line 52 *	1	
A	US 4 615 947 A (GOOSSENS JOHN C) 7 October 1986 (1986-10-07) * claims 1-11 * * column 7, line 41 - column 8, line 35 *	1	
A	EP 0 244 952 A (TORAY SILICONE CO) 11 November 1987 (1987-11-11) * claims 1-7 *	1	
A	EP 0 207 634 A (TORAY SILICONE CO) 7 January 1987 (1987-01-07) * claim 1 *	1	TECHNICAL FIELDS SEARCHED (Int.Cl.7)
A	WO 91 14747 A (COURTAULDS COATINGS HOLDINGS) 3 October 1991 (1991-10-03) * claim 1 *	1	C09D C09J C08L
A	EP 0 877 068 A (GEN ELECTRIC) 11 November 1998 (1998-11-11) * claim 1 *	1	
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 10 December 2001	Examiner Depijper, R
CATEGORY OF CITED DOCUMENTS		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document			

EPO FORM 1503 03 82 (P04C01)

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 00 30 4873

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
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10-12-2001

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 3671483	A	20-06-1972	BE 777469 A4	29-06-1972
			CA 972890 A1	12-08-1975
			DE 2160669 A1	06-07-1972
			FR 2120111 A6	11-08-1972
			GB 1332840 A	03-10-1973
			JP 53014580 B	18-05-1978
			US 3794556 A	26-02-1974
US 5458980	A	17-10-1995	US 5424357 A	13-06-1995
			DE 69411133 D1	23-07-1998
			DE 69411133 T2	12-11-1998
			EP 0656408 A2	07-06-1995
			JP 7207244 A	08-08-1995
US 4615947	A	07-10-1986	DE 3688645 D1	05-08-1993
			DE 3688645 T2	20-01-1994
			EP 0221148 A1	13-05-1987
			JP 2509923 B2	26-06-1996
			JP 62502623 T	08-10-1987
			WO 8606399 A1	06-11-1986
EP 0244952	A	11-11-1987	JP 1722651 C	24-12-1992
			JP 4011594 B	28-02-1992
			JP 62236880 A	16-10-1987
			JP 1753764 C	23-04-1993
			JP 4039507 B	29-06-1992
			JP 62280279 A	05-12-1987
			JP 1672909 C	12-06-1992
			JP 3034788 B	23-05-1991
			JP 63033474 A	13-02-1988
			DE 3769836 D1	13-06-1991
			EP 0244952 A2	11-11-1987
			US 4749741 A	07-06-1988
EP 0207634	A	07-01-1987	JP 1789851 C	29-09-1993
			JP 4075944 B	02-12-1992
			JP 61278582 A	09-12-1986
			DE 3680721 D1	12-09-1991
			EP 0207634 A2	07-01-1987
			KR 9310439 B1	25-10-1993
			US 4681636 A	21-07-1987
WO 9114747	A	03-10-1991	SG 152094 G	17-03-1995
			AU 651096 B2	14-07-1994
			AU 7577391 A	21-10-1991
			BR 9106209 A	23-03-1993

EPO FORM P4459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 00 30 4873

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

10-12-2001

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
WO 9114747	A		CA 2078144 A1	28-09-1991
			DE 69102535 D1	21-07-1994
			DE 69102535 T2	05-01-1995
			DK 521983 T3	14-11-1994
			EP 0521983 A1	13-01-1993
			ES 2056645 T3	01-10-1994
			FI 924303 A	25-09-1992
			WO 9114747 A1	03-10-1991
			HK 134794 A	09-12-1994
			JP 3205335 B2	04-09-2001
			KR 175648 B1	01-05-1999
			NO 303643 B1	10-08-1998
			PT 97186 A ,B	29-11-1991
			US 5290601 A	01-03-1994
EP 0877068	A	11-11-1998	EP 0877068 A2	11-11-1998
			JP 11043646 A	16-02-1999